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Preparation of a Chemically Stable Polysulfone-based Anion Exchange Membrane Using DABCO as the Quaternization Agent

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The anion exchange membrane is crucial to the fuel cell development. In this paper, polysulfone was firstly chloromethylated via in-situ generation of chloromethylether which is known as a carcinogenic. 1,4-diazabicyclo[2.2.2]octane (DABCO) was used as the quaternization agent. The rigid cage structure of DABCO molecule prevents the Hofmann elimination reaction from occurring, thus the thermal stability of anion exchange membrane was improved. The membranes with various degree of substitution (DS) were obtained and 106 % DS exhibited a highest ionic conductivity of 0.046 Scm^{-1} at 60°C and 100 % relative humidity. The maximum power output of single cell using hydrogen and oxygen reached 114 mWcm^{-2} . The good electrochemical performance and less harmful preparation procedures make QDPSU a promising membrane material for anion exchange membrane fuel cells.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have dominated the fuel cell research and development for decades. In the process of this study, Bertei has tried to improve membrane fuel performance by decreasing central membrane thickness and porosity (Bertei et al., 2011). Five catalysts showed better electrochemical stability of the support than the commercial high-surface-area reference catalyst while the stability of the Pt particles was better for one of them, catalyst Pt/CB3 (Kaluža et al., 2015). Their commercialization, however, is still hindered by the high cost of catalysts and Nafion® membrane materials. AAEMFCs are the high pH counterpart to the acidic PEMFCs due to the presence of sulfonic acid functional group. The alkali medium in AAEMFCs offers less corrosive electrolyte which allows the use of non-noble metal, chemically modified carbon as catalyst and alternative membrane materials (S. Lu et al., 2008). Thus, the cost of AAEMFCs can be significantly reduced. In addition, the fuel cross-over from the anode is eased due to the reversed osmotic drag and facile electrode reaction.

A major concern on AEMs is the chemical stability of QA groups especially when the temperature exceeds 60°C . The main degradation routes of QA groups are via direct nucleophilic displacement reaction and Hofmann elimination reaction (Varcoe et al., 2006). A number of investigations using quaternary salt tethered with long alkyl chain reported excellent chemical stability towards alkali at elevated temperatures due to the high electron density and steric shielding around the β -Hs. 1,4-diazabicyclo[2.2.2]octane (DABCO) has a unique rigid cage structure which prevent the β -Hs and the N atoms forming the anti-periplanar conformation required for facile Hofmann elimination to occur (Varcoe et al., 2014).

In this detailed study of QDPSU characterizations, DABCO was also used as the quaternization agent to improve the thermal stability after polysulfone was chloromethylated through in-situ generation chloromethylether which is known as carcinogenic. Both of using DABCO and in-situ generation of chloromethylether can significantly reduce the exposure risk of human to toxic substance, thus such preparation procedures benefit the scaling up production.

2. Experimental

2.1 Synthesis of quaternary DABCO polysulfone

The synthesis of QDPSU was described previously (Wang et al., 2011) which includes chloromethylation and quaternization reactions. 10 g (2.26 mmol) polysulfone (P-1700, Udel) was dissolved in 400 cm³ (mL) of 1, 2-dichloroethane. 6.78 g (22.6 mmol) paraformaldehyde and 24.6 g (22.6 mmol) trimethylchlorosilane were added to the solution with magnetic stirring. Stannic chloride 1.178 (0.452 mmol) was added dropwise and the reaction proceeded for 12 to 48 hours at 50 °C, to produce different degrees of substitution of CM-PSU. The white CM-PSU was precipitated in high purity ethanol (99.9 %) to remove the excess of reactants. The product was purified by dissolving in dimethylacetamide (DMAc), filtering and precipitating with distilled water several times. After that treatment, the product was dried in high vacuum to remove any residual solvent and kept in a vacuum before further use.

In order to avoid producing cross-linked QDPSU which is not soluble in DMAc, the quaternization at a different degree of substitution (DS) was completed by adding CM-PSU and DABCO in DMAc in a molar ratio of 1 (-CH₂Cl): 5 (DABCO). The mixture was stirred at 80 °C for 14 h, whereupon the product was precipitated using diethyl ether and dried at 60 °C in vacuum.

2.2 Thermo-gravimetric analysis

Thermo-gravimetric analysis (TGA) was performed on a TGA Q500 (TA instrument) using samples (20 mg) placed in a ceramic crucible. Samples were heated from room temperature to 600 °C at a rate of 5 °C min⁻¹ under flowing nitrogen (30 mL min⁻¹).

2.3 Swelling behaviour and water uptake

Swelling degree and water uptake were calculated using the equations from literatures (X. Wang et al., 2012; M. Mamlouk et al., 2011). Each sample was measured three times under identical conditions.

$$\text{Water uptake} = (m_{\text{wet}} - m_{\text{dry}}) / m_{\text{dry}} \times 100 \% \quad (1)$$

$$\text{Swelling degree} = (\delta_{\text{wet}} - \delta_{\text{dry}}) / \delta_{\text{dry}} \times 100 \% \quad (2)$$

where m_{wet} and δ_{wet} are the weight and cross-sectional thickness of fully hydrated membrane respectively and m_{dry} and δ_{dry} are the weight and cross-sectional thickness of fully dehydrated membrane respectively. The weight and thickness of samples were taken in the OH⁻ form when they were fully hydrated and dried, respectively. The drying of samples was carried out by placing them in a container fully filled with nitrogen gas for 1 h at 55 °C.

2.4 SEM and EDX

A low vacuum environmental scanning electron microscopy (ESEM, JSM-5300LV, Japan) incorporated with energy dispersive X-ray (EDX) spectroscopy was used to investigate the morphology and microstructure of membrane. The membrane was immersed in liquid N₂ for 10 min and was then broken off to investigate the morphology of membrane cross-section.

2.5 Ionic conductivity measurement

A four-point probe technique was used in a home-made cell for membrane conductivity (in-plane) measurement and detailed procedures were described in previous report (Mamlouk et al., 2011). All samples were cut into 1.0 cm wide, 5.0 cm long strips and placed on the platinum foil with 0.5 cm gap between them. AC impedance measurements were carried out at frequencies between 1 and 20 kHz with an oscillating amplitude of 10 mV. The polymer membranes were held at the desired temperature for 30 min to reach steady state under N₂ atmosphere. The N₂ gas humidifier was maintained at 10 °C higher than the conductivity cell to keep 100% relative humidity (RH).

2.6 MEA fabrication and fuel cell test

For preparing the electrode, catalyst inks for both anode and cathode were prepared by dispersing catalyst (40 wt % Pt/C electrocatalyst from Johnson Matthey) with 8 wt % of QDPSU solution (6 wt %) in DMAc. Then, the mixture was ultra-sonicated for 40 minutes. The ink was sprayed onto SGL 25BA carbon paper with 0.5 mg cm⁻² metal loading of catalyst. The MEA was then cold-pressed under a pressure of 120 kg cm⁻². The fuel cell performance measurement was conducted using a single cell with 1.0 cm² stainless steel serpentine flow field. H₂ and O₂ were fed into the single cell at flow rates of 80 cm³ min⁻¹ for the anode and 100 cm³ min⁻¹ for the cathode, respectively. Humidifiers were maintained at 10 °C higher than cell temperature to ensure 100 % RH at the cathode. Polarization curves were recorded using a sweep at a scan rate of 5 mV s⁻¹ by employing an Autolab 302N potentiostat until stable performance was reached.

3. Results and discussion

3.1 Reaction time

In Fig. 1, the degree of substitution (DS) was extracted from NMR results by using the method described previously (Wang et al., 2012). The DS of QDPSU in this study increased with increased time of reaction. The obtained DS of CM-PSU were 58 %, 80 %, 106 % and 180 % for reaction times of 8h, 14h, 24h and 48 h, respectively. The DS of CM-PSU increases in a logarithm pattern rather than linear pattern which indicates the reaction rate decreased during the reaction due to the steric effect of chloromethylated groups. The mechanical property of the membrane with 180 % DS was found too brittle to use in the presence of water. Thus, it was not possible to characterize it.

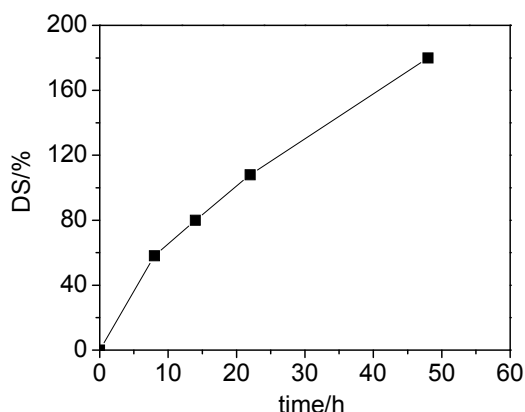


Figure 1: Time dependence of the degree of substitution

3.2 Thermal stability analysis

The thermal stability of QDPSU-DS106 and PSU were examined using TGA as shown in Fig.2. Before the experiment, the QDPSU was converted to the OH- form. For QDPSU, the weight loss under 100 °C is mainly attributed by free-water loss. At a temperature range between 100 and 200 °C, the bonded water and QA group started decomposing. The decomposition of QDPSU backbone occurred at the temperatures higher than around 200 °C. The above data indicates that QDPSU is thermally stable under the operating temperature range of low temperature fuel cells (< 100 °C) which is suitable for the AAEMFC application.

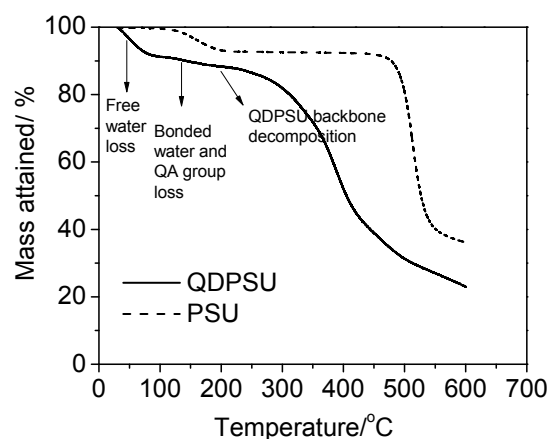


Figure 2: Thermo gravimetric analysis of PSU and QDPSU

3.3 Swelling behaviour and water uptake analysis

In Table 1, the mechanical strength, swelling degree and water uptake of all samples are listed. The pristine PSU film had a maximum strength of 28.8 MPa. With increasing DS, a trend of decreasing on maximum strength of membrane film was found in our result whilst the swelling degree and water uptake of membranes were increasing significantly to up to 24 ± 2 and 81 ± 6 %, respectively. This is caused by the increasing number

of hydrophilic functional groups (quaternary DABCO groups) in the polymer matrix. In addition, the swelling degree and water uptake showed highly dependency with each other.

Table 1: Physical properties of QDPSU membranes

Samples	Maximum strength /MPa	Maximum Extension /mm	Swelling degree/ %	Water uptake/ %
QDPSU-DS106	20.2	1.9	24±2	81±6
QDPSU-DS80	26.0	2.4	12.7±1	46.1±4
QDPSU-DS58	26.8	2.3	6.3±1	19.7±3
PSU	28.8	2.8	-	-

The solubility study of PSU, CM-PSU and QDPSU was conducted by immersing a small piece of membrane samples in different solvents and left overnight at room temperature. The solubility of different polysulfone materials are listed in Table 2. All samples were dissolved completely in dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO). However, the product QDPSU is insoluble in low-boiling point solvents used in this study. The low-boiling point of solvents indicates the bonds between molecules are weak which is unable to split the QDPSU polymer molecules. Based on the solubility study, the solvent for catalysts ink preparation was DMAc.

Table 2: Solubility of PSU, CM-PSU and QDPSU in different solvent at room temperature

Sample	PSU	CM-PSU	QDPSU
DI-water	-	-	-
Ethanol	-	-	-
Toluene	-	-	-
Chloroform	+	+	-
Tetrahydrofuran	+	+	-
Dimethylacetamide	+	+	+
Dimethyl sulfoxide	+	+	+

3.4 SEM and EDX analysis

The morphology of QDPSU membrane was investigated using SEM. Figure 3a and b show that the surface and cross-section of membrane are dense and non-porous structure. The EDX element mapping of chlorine represents functional QA group and sulphur represents polysulfone backbone is shown in Figure 3c and d. These elements were dispersed homogeneously through the cross-section of the membrane. These results reveal that the obtained AAEM was uniform. These images indicate that the membrane is an effective separator for the gaseous reactant on the anode and the cathode and it can provide continuous pathways for ion conducting.

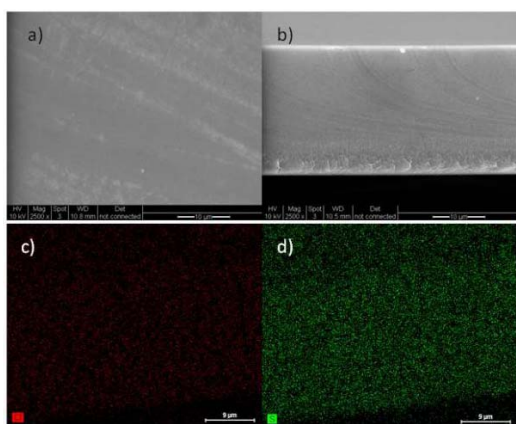


Figure 3: SEM images of QDPSU-DS106 a) surface, b) cross-section; element mapping of QDPSU membrane c) chlorine and d) sulphur

3.5 Ionic conductivity

The ionic conductivity of different DS of QDPSU was measured in a temperature range of room temperature to up to 60 °C under 100 % RH (as shown in Fig. 4). Ionic conductivities of all membranes increased with increasing temperature. At 50 °C, the ionic conductivities of QDPSU-DS58, QDPSU-DS80 and QDPSU-DS106 were 0.016, 0.027 and 0.039 S cm⁻¹, respectively.

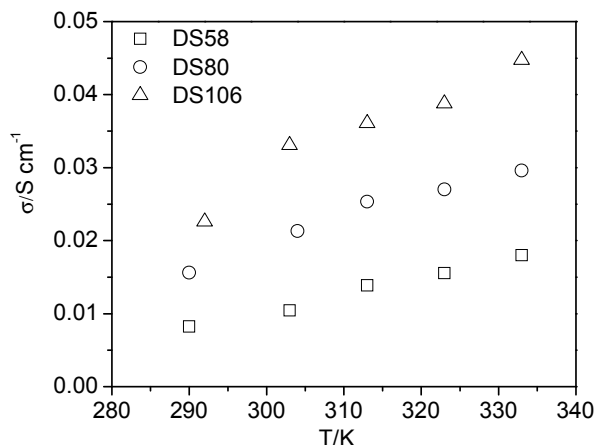


Figure 4: Ionic conductivities of QDPSU membranes at different temperatures and 100 % RH

3.6 MEA performance

The MEA was fabricated with QDPSU (DS106) membrane and commercial Pt/C catalyst. In Fig. 5, the open circuit voltage was above 1.0 V which indicates the QDPSU membrane was effective separator for hydrogen and oxygen. The maximum power output of the MEA was 114 mW cm⁻² at 60 °C. Such performance was similar to other reports using QAPSU membrane (J. Pan et al., 2010). It is worth of mentioning that the MEA hadn't been optimized in term of the ionomer content, catalyst and operating conditions. There is still great potential for improving the QDPSU based fuel cell performance.

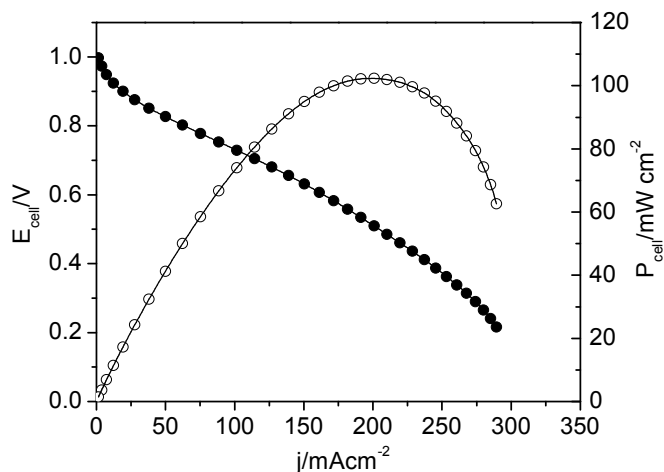


Figure 5: The fuel cell performance at 60 °C using DS106 QDPSU and 0.5 mg cm⁻² metal loading for both anode and cathode

4. Conclusions

Quaternary DABCO polysulfone was successfully prepared with different degree of substitution via a safe and scalable route. The cross-linking of polysulfone was suppressed by adding five times molar ratio DABCO salt than polysulfone. The ionic conductivity of resulted anion exchange membrane reached as high as 0.046 S cm⁻¹. Other properties (e.g. mechanical strength) met the basic demand for fuel cell applications. The maximum power output was 114 mW cm⁻². Therefore, QDPSU is a promising membrane candidate for AAMEFCs.

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